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ORIGINAL ARTICLE

Mechanochemically improved surface properties of activated carbon cloth for the removal of As(V) from aqueous solutions

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Abstract Modified activated carbon cloth is prepared by mechanochemical modification of viscose rayon carbon cloth. The effects of different milling atmospheres, in the air and inert conditions, were investigated. Changes in kind and number of acidic and basic surface groups on the surface of activated carbon cloth, upon modification, as well as before and after the sorption of arsenic were determined. Higher number of basic groups responsible for the removal of arsenic ions was achieved by modification under inert conditions. Breakage and collapse of cylindrical fibers, decrease of particle sizes, change in the shape and consistency of the particles, as well as increase of microstructural disorder i.e. the loss of turbostratic structure occurred upon milling. pH_{PZC} values increased from 4.46 to 5.04 and 5.77 after the air and inert milling, respectively. Adsorption followed pseudo second order kinetics with chemisorption as rate-controlling step. Langmuir isotherm best fit the equilibrium data and maximum adsorption capacity is 5.5 mg g^{-1} at a pH value close to 7.0, typical for groundwater. The mechanism of arsenic adsorption onto activated carbon cloth milled in inert atmosphere involved electrostatic and dispersive interactions between arsenic ions and carbon particles in wide pH range (from 2 to 10).

1. Introduction

Contamination of water with arsenic either from natural or from anthropogenic sources has become one of the major environmental problems due to its toxicity, non-biodegradability and tendency of accumulation in living organisms (Smedley and Kinniburgh, 2002). Arsenic is one of the highly harmful heavy metals, which can seriously affect human health. In natural water, inorganic arsenic is

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predominantly found in +3 and +5 oxidation states and their relative distribution is influenced by pH and the redox condition of water environment. In surface waters, i.e. under oxidizing conditions, the predominant species are pentavalent arsenate mainly present in the oxyanionic forms (H_3AsO_4, $H_2AsO_4^-$ and $HAsO_4^{2-}$). On the other hand, trivalent arsenite (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$) is more prevalent in anaerobic aquatic environments under mildly reducing conditions, such as groundwaters (Kuriakose et al., 2004; Xu et al., 2002).

Among various conventional methods (Jain and Ali, 2000; Muñiz et al., 2009; Zhang et al., 2007), adsorption has been one of the most promising for the removal of arsenic ions from wastewater due to high efficiency, easy handling, cost effectiveness and availability of various adsorbents. Several types of natural and synthetic adsorbents such as carbon-based material (activated carbons) (Chuang et al., 2005; Lee, 2010), clay minerals (Lin and Puls, 2000), zeolites (Bilici Baskan and Pala, 2011), agricultural and industrial wastes (Altundoan et al., 2002; Amin et al., 2006) can be effectively used for removal of arsenic ions from contaminated water. However, most of them show the low adsorption capacity and/or slow kinetic of adsorption, ineffectiveness for high metal ion concentration and unfavorable cost/efficiency ratio which limit their application deeply.

In recent decades, carbon-based materials i.e. activated carbon cloths are widely used for decontamination of water from heavy metals because of their high adsorption capacities as well as nontoxicity. Activated carbon cloths belong to a new class of adsorbents developed for the wastewater treatment. The high surface area (between 1000 and 2100 $m^2 g^{-1}$), small fiber diameter (which minimizes diffusion limitations), faster adsorption kinetics, easy regeneration and easy pore accessibility, narrow pore size distribution, great adsorption capacity for low concentrations of adsorbates and specific surface properties make this material to be superior compared to granular and powder activated carbon (Bhati et al., 2014). Various synthetic and natural precursors, such as polyacrylonitrile (PAN), polyphenol, viscose rayon, cellulose phosphate, phenolic resins and pitch based fiber can be used for preparation of the activated carbon cloths by chemical or physical activation (Bhati et al., 2014). Among them, cellulosic polymers (cotton, rayon and jute) are the most prominent precursors because of their low cost, commercial availability, high microporosity and biodegradability (Bhati et al., 2014; Phan et al., 2006).

Extensive studies demonstrated that activated carbon cloths can be successfully used for removing heavy metals as well as organic pollutants from wastewater (Kadirvelu et al., 2000; Lee, 2010; Leyva-Ramos et al., 2011; Métivier-Pignon et al., 2003; Phan et al., 2006). Their adsorption properties are highly dependent on the type of precursors i.e. their specific surface area, pore volume, pore size distributions and surface chemistry which is mainly determined by the surface oxygen- and nitrogen-containing groups (Venckatesh and Amudha, 2010).

Different studies have demonstrated that surface properties of activated carbon cloths and consequently its metal binding ability can be significantly enhanced by various physical and (electro)chemical methods of modification (Kodama et al., 2002; Lee et al., 2015; Leyva-Ramos et al., 2011; Moreno-Castilla et al., 2004; Park and Kim, 2005; Park et al., 2003; Sun et al., 2013; Zhang et al., 2010). Very few papers regarding the use of activated carbon cloth for the removal of arsenic anions exist in the literature. For example, Lee et al. (2015) showed that adsorption ability of activated carbon fibers (ACF) for removing arsenic ions from aqueous solutions could be significantly enhanced by impregnation with iron oxide. Zhang et al. (2010) demonstrated that ACF impregnated with nano-sized magnetite have about eight times higher adsorption capacity for arsenic ions compared to the unmodified ACF. Also, Sun et al. (2013) reported that manganese oxides modified ACF had a higher adsorption capacity for arsenic ions compared to raw ACF. The authors of the abovementioned studies have reported that the difference in the adsorption behavior of unmodified and modified ACF is a result of different surface properties of the material before and after modification (Lee et al., 2015; Sun et al., 2013; Zhang et al., 2010). So, all of these results refer to the use of impregnation substances in the treatment of activated carbon cloths in the removal of arsenic species.

In the last few decades, mechanical milling has proven to be successful method for the improvement of adsorption properties of different materials. In regard to the chemical methods, it was found to be superior because it is inexpensive and environmentally friendly method of modification. In limited number of studies the influence of mechanochemical milling on the microstructure and adsorption properties of different organic and inorganic materials (mainly clay minerals, metal hydrides, etc.) have been investigated (Kumrić et al., 2013; Montinaro et al., 2007; Nenadović et al., 2009; San Cristóbal et al., 2010). However, to our best knowledge, in the available literature there is no information about mechanochemical modification of the activated carbon cloths.

Therefore, the aim of present study was to investigate the possibility of improving of adsorption behavior of activated carbon cloth by mechanical milling under different atmospheres (air and argon) and to investigate its usability for removing arsenic ions from wastewater. The effects of various experimental parameters such as contact time, initial metal-ion concentration, solution pH and amount of adsorbent were investigated. The adsorption behavior of the arsenic ions onto activated carbon cloth samples was correlated with changes in the surface properties induced by milling.

2. Experimental

2.1. Sample preparation

The viscose rayon carbon cloth used in this study as initial adsorbent is manufactured in "Vinča" Institute of Nuclear Sciences (Serbia) (Babić et al., 2002). Mechanochemical activation was used as a method for modification of activated carbon cloth. Milling process was performed with stainless balls (diameter 6 mm) in stainless vial (60 cm^3) of Turbula Type 2TC Mixer under air and argon atmosphere with ball to powder (BPR) ratio fixed at 20:1 and milling time of 20 h. The milling conditions were determined arbitrarily because there is no literature data about mechanochemical activation of activated carbon cloth. The focus of the research was to investigate the influence of the atmosphere in which the sample was mechanochemically modified in order to improve its adsorption properties. The unmodified activated carbon cloth (cut in little pieces) was denoted as ACC, while activated carbon cloths mechanochemically modified under air and argon atmosphere were denoted as M-ACC-Air and M-ACC-Ar, respectively.

2.2. Material characterization

Microstructure and morphology of (un)milled samples have been investigated by XRD, PSD and SEM. The specific surface area and pore size distribution were determined by BET analysis, while surface chemistry was investigated by FT-IR and Boehm titrations method for determination of surface functional groups and batch equilibrium method for determination of point of zero charge (pH_{PZC}).

The XRD analyses of the samples were conducted using Siemens D-500 diffractometer with filtered Cu Kα radiation (λ = 1.5406 Å), over the range of 2θ from 2 to 90°, at the scanning speed of 0.02 step/s.

The quantitative PSD analyses of the samples dispersions were conducted using Malvern 2000SM Mastersizer laser

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scattering particle size analysis system with specified resolution range from submillimeter to 2 mm.

The SEM analyses of the samples were conducted using VEGA TS 5130, Tescan SEM equipped with the EDS detector.

The specific surface area and pore size distribution of unmilled and milled samples were determined by nitrogen adsorption-desorption at 77 K using a Sorptomatic 1990 Thermo Finnigan device. Prior to adsorption, the samples were degassed for 4 h at room temperature under vacuum, additionally 8 h at 383 K and finally 12 h at 523 K at the same residual pressure. Various models and appropriate software ADP Version 5.17 CE Instruments were used to analyze the obtained isotherms. The total pore volume (V_{tot}) was calculated by applying Gurevitsch's rule (Gregg and Sing, 1967) at relative pressure $p/p_0 = 0.95$ (p and p_0 represent the equilibrium and saturation pressures of nitrogen at the temperature of adsorption). The specific surface area of samples, S_{BET}, was calculated according to the Brunauer, Emmett, Teller method, from the linear part of the isotherms (Sing, 2001). Micropore volumes were obtained using the Dubinin-Radushkevich method (V_{mic}-DR) (Dubinin, 1975) and Horvath-Kawazoe method (V_{mic}-HK) (Horváth and Kawazoe, 1983).

The FT-IR analyses of the samples were performed by PerkinElmer Spectrum Two FT-IR spectrometer using the pressed KBr pellets (1:100) technique.

The amounts of acidic and basic surface functional groups of adsorbents were determined by Boehm's titrations method (Goertzen et al., 2010).

pH_{PZC} was determined by batch equilibration method, previously described by Čerović et al. (2007).

2.3. Batch adsorption experiments

All the chemicals used in this study were of analytical-reagent grade. Arsenic stock solutions (H_3AsO_4 in 0.5 M HNO_3), sodium hydrogen carbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) were procured from Merck (St. Louis, MO, USA). Sodium hydroxide (NaOH) and nitric acid (HNO_3) were procured from LachNer (Brno, Czech Republic).

The adsorption of arsenic ions on the ACC and M-ACC-Ar was studied by batch technique. Working arsenic solutions, with concentrations in the range of 2.5–10.0 mg dm^{-3}, were prepared by diluting arsenic standard solutions (1000 mg dm^{-3}). The pH of the working solution was adjusted by adding a small amount of 0.1 mol dm^{-3} HCl or NaOH.

Batch adsorption experiments were carried out at room temperature using 20 cm^3 of metal ion solution and 0.02 g of adsorbents (unmilled and milled). The samples in closed polyethylene bottles were shaken on the laboratory shaker (Promax 2020, Heidolph, Schwabach, Germany) for 15 h at a stirring speed of 200 rpm and then filtered through a 0.45 μm microporous membrane filter (membrane Solutions LLC, TX, USA). The concentrations of arsenic ions in each aliquot were determined by atomic absorption AAS Aanalyst 700/Perkin-Elmer spectrometer.

The influence of contact time (30 min–72 h), solution pH (2–10), initial metal-ion concentration (2.5–10.0 mg dm^{-3}) and amount of adsorbent (0.25–2.5 g dm^{-3}) on the adsorption of arsenic ion was investigated.

The amount of arsenic ion adsorbed at equilibrium per unit mass of adsorbent, q_e (mg g^{-1}), and the removal efficiency, E (%), were calculated using the following relations:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

$$E = 100\left(\frac{C_i - C_e}{C_i}\right) \tag{2}$$

where C_i and C_e (mg dm^{-3}) are the initial and the equilibrium concentration of arsenic ion in solutions, respectively, V is the volume of the solution (dm^3) and m is the mass of adsorbent (g).

The experimental data for arsenic ions adsorbed onto investigated adsorbent were approximated by the linear and nonlinear Langmuir and Freundlich isotherm models (Eqs. (3)–(6), respectively) (Kumrić et al., 2013):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, \tag{3}$$

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e}, \tag{4}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

$$q_e = K_F C_e^{1/n} \tag{6}$$

in which q_m is the monolayer adsorption capacity of adsorbent (mg g^{-1}), and K_L, K_F and n are the Langmuir and Freundlich constants of adsorption.

The linear and nonlinear forms of pseudo-first-order and the second-order kinetic model (Eqs. (7)–(11), respectively) and intraparticle diffusion model Eq. (11) were applied for determination of adsorption mechanism of arsenic ions onto ACC adsorbents (Hameed et al., 2007; Mouni et al., 2011):

$$\ln(q_e - q_t) = \ln q_e - K_{pf} t, \tag{7}$$

$$q_t = q_e(1 - e^{-K_{pf} t}) \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{K_{ps} q_e^2} + \frac{1}{q_e} t \tag{9}$$

$$q_t = \frac{K_{ps} q_e^2 t}{1 + K_{ps} q_e t} \tag{10}$$

$$q_t = K_{id} t^{0.5} + a \tag{11}$$

where q_t is the amount of arsenic ions adsorbed per unit mass of adsorbent (mg g^{-1}) at time t (min), K_{pf}, K_{ps} and is K_{id} are the pseudo-first-order (min^{-1}), pseudo-second-order (g mg^{-1} min^{-1}) and intraparticle diffusion (mg g^{-1} $min^{-1/2}$) equilibrium rate constant, respectively, and a (mg g^{-1}) is a constant which shows the boundary layer or mass transfer effect.

3. Result and discussion

The adsorption of heavy metal ions from aqueous solutions onto carbon-based materials essentially depends on the specific surface area, the surface chemistry i.e. acidic and basic surface functionalities as well as various experimental conditions (Tuna et al., 2013). Therefore, in order to explain adsorption of arsenic ions onto activated carbon cloth, the surface chemistry, surface area and microstructure are important to be considered (Daud and Houshamnd, 2010).

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The surface chemistry of carbon-based materials depends on the nature of starting material (precursor) from which the carbon-based material is obtained, activation process or post-activation treatment in which oxygen, hydrogen and other elements can be introduced into the structure, Fig. 1 (Afkhami et al., 2008; Harry et al., 2007; Perrard et al., 2012; Shim et al., 2001).

The changes in the amounts of the acidic and basic surface groups of ACC induced by milling under different atmospheres were determined by Boehm titrations method (Table 1). On the surface of ACC the most prominent are the phenolic groups (95.3%), then carboxylic groups (4.4%), while the presence of lactonic groups is negligible (below 0.3%). The negligible number of lactonic groups has been observed in other carbon-based materials also (Harry et al., 2007).

Milling of ACC in air and argon atmospheres leads to the increase in the total number of acidic and basic functional groups. Increase in the total number of acid groups on the surface of the M-ACC-Air is the result of the significant increase in the number of phenolic groups (from 2.8753 mmol g^{-1} to 3.9833 mmol g^{-1}) and a slight increase of the number of lactonic groups (from 0.0080 mmol g^{-1} to 0.0107 mmol g^{-1}) while the number of carboxylic groups is reduced (from 0.1340 mmol g^{-1} to 0.0967 mmol g^{-1}). Increase in the number of acidic groups upon milling can be attributed to chemisorption of oxygen on the unsaturated carbon atoms at the edges of the graphene layers and in basal plane defects (Figueiredo, 2013). Strelko et al. (2002) also reported increase in the number of phenolic and lactonic groups on the surface of carbon-based material after oxidation with hot air.

The same trend of increasing the number of acidic groups, namely phenolic and lactonic groups, and the reduction of the carboxylic groups with milling has been observed for milling under inert atmosphere, M-ACC-Ar (Table 1). However, milling under inert atmosphere had a greater influence on the total number of basic groups; greater increase in the number of basic groups in M-ACC-Ar in regard to M-ACC-Air can be attributed to the absence of possibility for oxygen chemisorptions which is responsible for the formation of carbon-oxygen groups that possess acidic character. Carbon based materials with a greater number of basic surface groups show anionic exchange behavior, as previously reported by Boehm (Boehm, 1994).

However, the specific surface area and pore volume of materials influence the adsorption capacity and they are important parameters in adsorption mechanism (Daud and Houshamnd, 2010). So, the influence of mechanochemical milling under different atmospheres on the values of specific surface area and pore volume of ACC was investigated. Fig. 2 shows the nitrogen adsorption-desorption isotherms of ACC, M-ACC-Ar and M-ACC-Air. All three isotherms, according to classification proposed by Rouquerol et al. (1999) are type Ia, typical for microporous materials.

Indeed, the sharp increase of V_{ads} in low relative pressures region somewhat extended until the relative pressure of less than 0.15, and existence of long flat plateau and complete

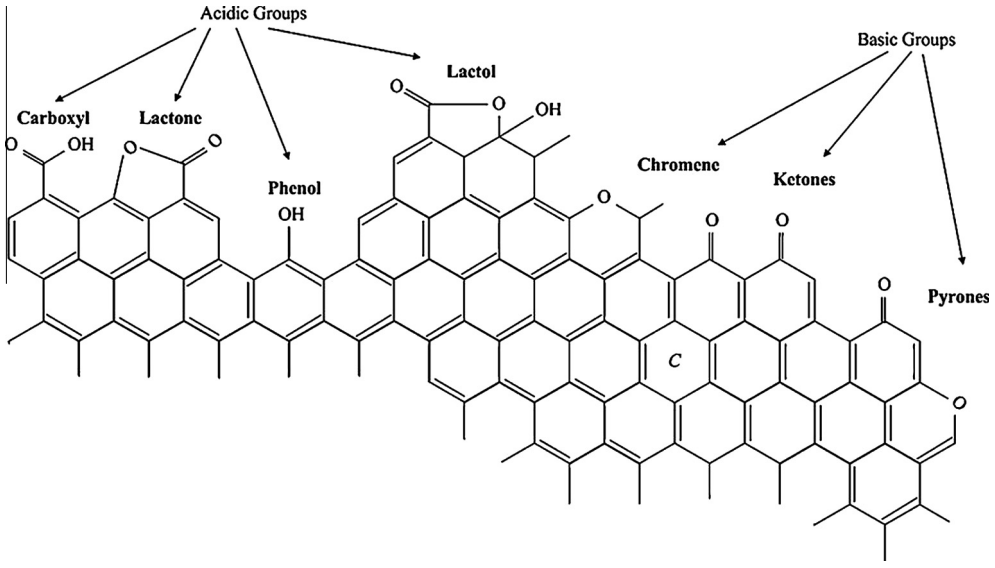

Figure 1 Acidic and basic surface functionalities on a carbon basal plane (Montes-Morán et al., 2004).

Table 1 Amounts of various oxygen-containing functional groups (mmol g^{-1}) of ACC, M-ACC-Air and M-ACC-Ar.

Adsorbent	Basic groups (mmol g^{-1})	Acidic groups (mmol g^{-1})	Carboxylic groups (mmol g^{-1})	Lactonic groups (mmol g^{-1})	Phenolic groups (mmol g^{-1})
ACC	0.1093	3.0173	0.1340	0.0080	2.8753
M-ACC-Air	0.1327	4.0907	0.0967	0.0107	3.9833
M-ACC-Ar	0.5260	3.8346	0.1060	0.0120	3.7166

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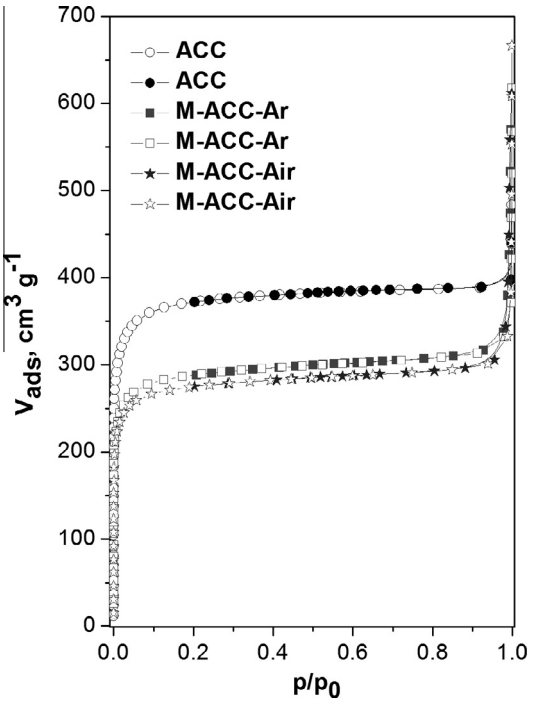

Figure 2 Nitrogen adsorption-desorption isotherm samples of ACC (circles), M-ACC-Ar (squares) and M-ACC-Air (stars). The empty symbols represent adsorption and the filled symbols represent desorption results.

reversibility of desorption brunch are typical for this isotherm type. The most noticeable change of obtained isotherms is the change in the plateau position, which is lower for milling samples compared to starting one. Obviously, milling process causes decrease in micropore volume, as both Dubinin-Radushkevich and Horvath-Kawazoe methods (Table 2) reveal. The level of decrease of V_{mic} is similar, but somewhat more pronounced for the sample milled in an air atmosphere. Exactly the same behavior is observed for the values of specific surface area changes.

Slight decrease in surface area and pore volume was observed by milling. Reduction in surface area and pore volume by wet oxidation has been reported by several researchers (El-sheikh, 2008; Gorgulho and Pereira, 2008; Lemus-Yegres et al., 2007; Tanada et al., 1999). This trend is attributed to one or a combination of reasons: pore blockage by oxygen and nitrogen surface groups, their electrostatic repulsion and wall erosion or destruction of micropore walls (converting to mesopores) (Álvarez et al., 2005; Gorgulho and Pereira, 2008; Jansen and Bekkum, 1994; Maroto-Valera et al., 2004; Moreno-Castilla et al., 1997; Strelko et al., 2002). Biniak et al. (1997) also showed that the surface chemistry of carbon-based materials has greater influence on the adsorption of inorganic compounds from aqueous solutions in regard to the materials porosity.

Considering that only M-ACC-Ar showed increased number of basic groups it was further studied for the removal of arsenic anions from aqueous solution. Thus, microstructural and morphological characterization was used to evaluate changes induced by milling under inert conditions.

3.1. Microstructural characterization

The XRD patterns of ACC and M-ACC-Ar are presented in Fig. 3a and b. The broad peaks located at the positions $2\theta = 24°$ and 44° correspond to the reflections from disordered graphitic (002) and (10*l*) planes (overlapped 100 and 101 planes) of turbostratic carbon structure, respectively (Tzeng et al., 2006; Walker, 1963). It means that structure is made from turbostratic groups (graphite microcrystallites, bound by cross-links), which consists of a several graphite layers nearly parallel and equidistant, but with random orientation of each layer typical for different carbonaceous materials (Coutinho et al., 2000). The changes of the ACC structure upon milling are revealed in the reduction of (002) and (10*l*) reflection intensities (Fig. 3b), suggesting the increase of structural disorder.

Fig. 4 presents the particle size distribution curves of ACC and M-ACC-Ar. The ACC has a polymodal distribution of particles in the range from 9 to 2000 μm, with mean particle sizes of 24.2 μm (~62%), 96.7 μm (~29%) and 472.2 μm (~8.8%); it is a result of ACC cutting into little pieces before milling. The milling leads to the drastic changes in the shape and width of the distribution curve; the M-ACC-Ar shows a quite narrow monomodal distribution of particles in the range from 0.2 to 20 μm with the mean particle size of ~4.7 μm.

Morphology of the as received ACC is presented on SEM micrographs, Fig. 5a and b. ACC is composed of multi-fiber cylindrical threads quite uniform in the shape and size, with external diameter of 19.6 μm. Grooves visible on the fibers

Table 2 The variation of values of specific surface area, S_{BET} and micropore volume, V_{mic}-DR and V_{mic}-HK and total pore volume, V_{tot}, for ACC, M-ACC-Ar and M-ACC-Air.

Adsorbent	S_{BET} ($m^2 g^{-1}$)	V_{mic}-DR ($cm^3 g^{-1}$)	V_{mic}-HK ($cm^3 g^{-1}$)	V_{tot} ($cm^3 g^{-1}$)
ACC	1470	0.549	0.572	0.606
M-ACC-Ar	1130	0.427	0.443	0.500
M-ACC-Air	1090	0.412	0.424	0.474

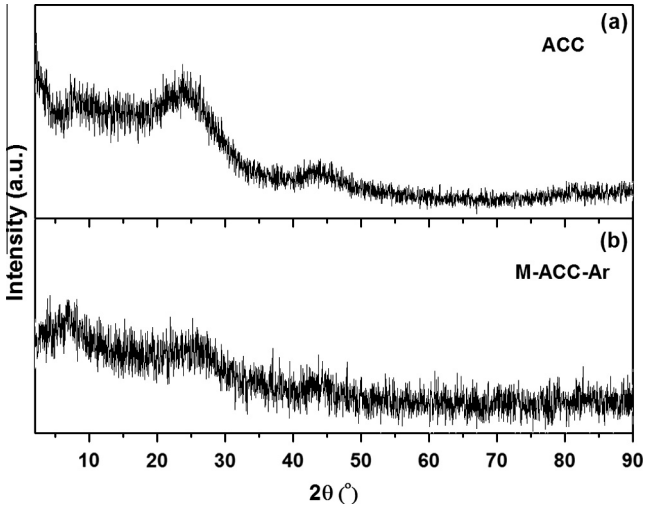

Figure 3 XRD patterns of ACC and M-ACC-Ar.

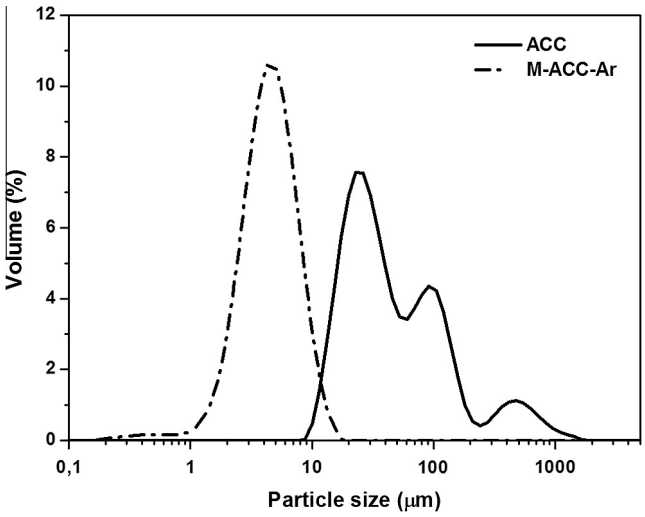

Figure 4 Particle size distributions of ACC and M-ACC-Ar.

surface were incurred during filature and their wideness is about 3 μm (Harry et al., 2007; Rodriguez-Reinoso et al., 2000; Shen et al., 2006, 2008; Wang et al., 2006). Tiny particles noticeable on the fibers surface are attributed to the adsorbed impurities such as steam and organic molecules from air (Harry et al., 2007; Rodriguez-Reinoso et al., 2000; Shen et al., 2006, 2008; Wang et al., 2006).

SEM images of M-ACC-Ar, shown in Fig. 5c and d, indicated the almost complete destruction of typical fibrous structure of ACC; the main effects are collapse and breakage of cylindrical fibers with decrease of particle sizes. Formed particles are micrometer-sized, irregular in shape, with sharp edges. Particles show tendency for gluing, forming agglomerates of few microns (Fig. 5c). Decrease of particle sizes should lead to the increase of surface area.

Similar microstructural changes were obtained by chemical modification of ACC (Harry et al., 2007; Perrard et al., 2012). Harry et al. (2007) showed that fibers of viscose-rayon activated carbon cloth after electrochemical oxidation with potassium chloride (as an electrolyte) were broken and probably become more fragile after severe oxidation (Harry et al., 2007). Also, Perrard et al. (2012) showed that chemical oxidation of ex-cellulose activated carbon cloth with sodium hypochlorite also leads to the fibers breaking (Perrard et al., 2012).

3.2. Adsorption study

3.2.1. Comparative study of adsorption of arsenic ions on ACC and M-ACC-Ar

In order to investigate the adsorption behavior of ACC and M-ACC-Ar, the batch adsorption experiments were carried out; the adsorption of arsenic ions on ACC and M-ACC-Ar was investigated by varying contact times (6, 24 and 48 h), keeping the concentration of arsenic-ion solution at 100 ppb (pH 6), Table 3.

The results presented in Table 3 show that M-ACC-Ar enables a more efficient removal of arsenic ions from aqueous

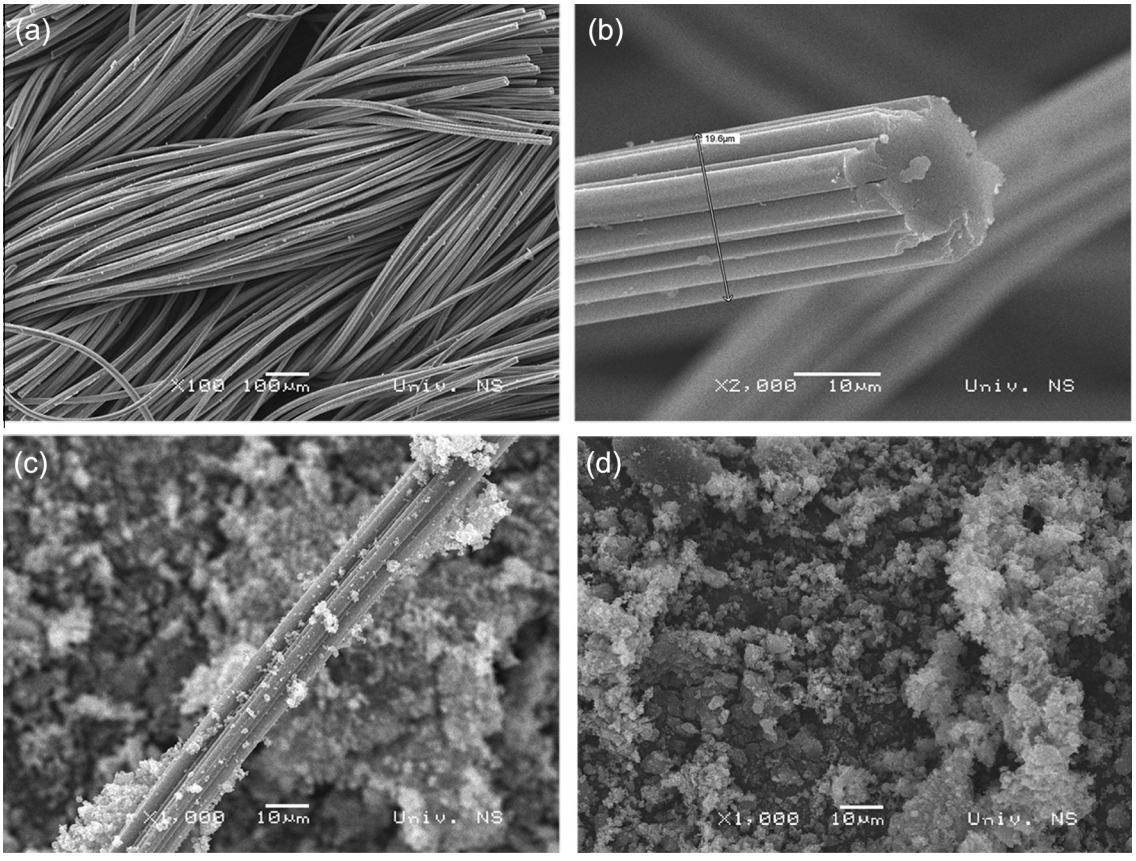

Figure 5 SEM images of (a, b) ACC and (c, d) M-ACC-Ar.

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Table 3 Effect of mechanochemical activation of the ACC on the removal of arsenic ions at different contact times.[a]

Heavy metal	Contact time	ACC E (%)	M-ACC-Ar E (%)
Arsenic ions	6 h	–	95.5
	24 h	21.0	98.1
	48 h	28.6	100.0

[a] Conditions: pH, 6; adsorbent concentration, 1 g dm^{-3}; and initial metal-ions concentration, 100 ppb.

solution than ACC. Considering that ACC, shows a low removal efficiency of arsenic ions (only 28.6% after contact time of 48 h) from aqueous solutions of low arsenic concentration of 100 ppb, the further experiments were directed toward examining adsorption ability of M-ACC-Ar.

3.2.2. Effect of contact time and initial concentration of metal ion

The effect of contact time and initial metal-ions concentration on the percentage removal of arsenic ion by M-ACC-Ar adsorbent is shown in Fig. 6.

The removal efficiencies of arsenic ions increase with an increase of contact time and attain equilibrium for 3 h for 2.5 mg dm^{-3} and 15 h for 5.0, 7.5 and 10.0 mg dm^{-3}; the percentages of arsenic ions removed at equilibrium contact time from the aqueous solution with different initial concentrations are 99.1%, 89.5%, 72.2% and 58.6%, respectively. The fast adsorption rate at first 30 min of adsorption indicates the importance of the surface on the adsorption process. The contact time of 15 h was further used.

Then, the removal efficiencies of the arsenic ions decrease with the increase of initial metal-ion concentration in aqueous solution Fig. 6; it can be attributed to the saturation of the available adsorption sites on the M-ACC-Ar. Also, the adsorption capacity, q_e, increased with increasing initial arsenic ion concentration due to increase in the driving force of the arsenic ions toward the adsorption sites on the M-ACC-Ar.

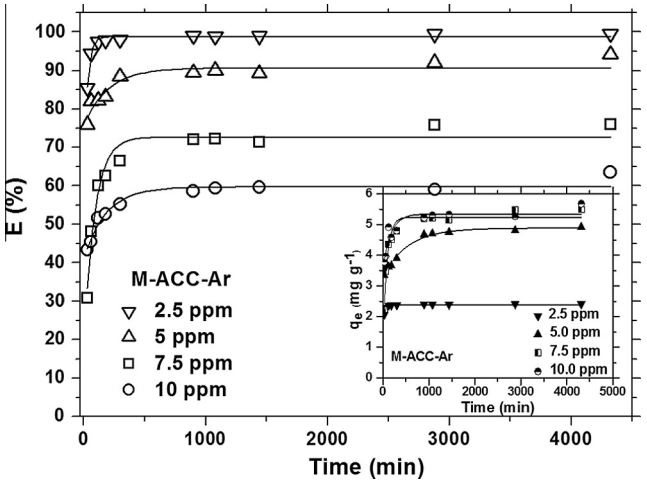

Figure 6 Effect of contact time and initial concentrations on the adsorption of arsenic ion on the M-ACC-Ar. Conditions: pH, 6; contact time, 15 h; stirring speed, 200 rpm.

3.2.3. Effect of adsorbent concentration

The effect of adsorbent concentration on the removal efficiency of arsenic ion by M-ACC-Ar was investigated by varying the amount of the M-ACC-Ar from 0.25 to 2.5 g dm^{-3}, keeping the arsenic ion concentration at 10.0 mg dm^{-3} and pH at 6 (Fig. 7).

The removal efficiency of arsenic ion increased rapidly with increase of adsorbent concentration (Fig. 7), due to the higher number of available active sites for the adsorption (Yao et al., 2014). For the complete removal of arsenic ions from 10.0 mg dm^{-3} (pH 6) solution, a maximum adsorbent concentration of 2.5 g dm^{-3} is required. However, taking into account that larger amounts of adsorbent increase the cost of wastewater treatment, adsorbent concentration of 1.0 g dm^{-3} was used for the rest of the experiments.

3.2.4. Effect of pH

The surface functional groups of adsorbents and speciation of arsenic ions in aqueous solution strongly depend on pH (Tuna et al., 2013). So the adsorption of arsenic ions on the M-ACC-Ar was investigated by varying solution pH from 2.4 to 10.1, Fig. 8. Adsorption of arsenic ions displayed strong pH dependence with the maximum removal efficiency in the low pH range.

Although the highest removal efficiency is achieved at pH 2, all parameters were investigated at pH 6 since arsenic is unique among the heavy metals: oxyanion forming elements due to their sensitivity to the redox conditions and to mobilization at a pH value close to 7.0 are typical for groundwater.

3.2.5. Adsorption isotherms

The adsorption study was conducted at a constant adsorbent concentration (1 g dm^{-3}) by varying the initial arsenic ion concentration from 2.5 to 10.0 mg dm^{-3} (pH 6). The obtained equilibrium data were analyzed by linear and nonlinear Langmuir and Freundlich isotherm models (Figs. S1 and S2, Supporting information) and the values of q_m, K_L, K_F, n and R are presented in Table 4. According to the values of R^2 for

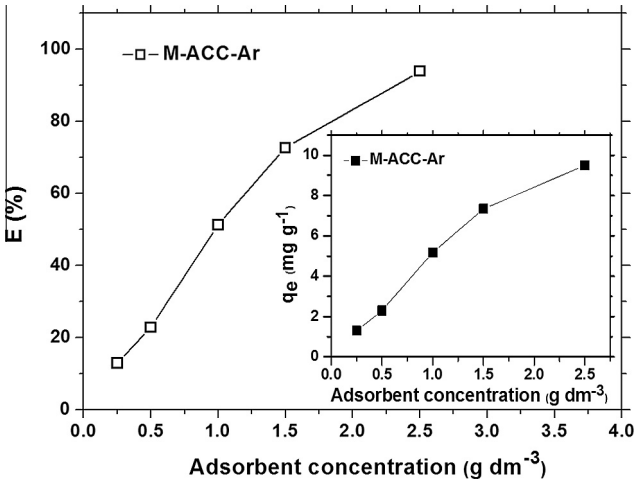

Figure 7 Effect of adsorbent concentration on the adsorption of arsenic ion on the M-ACC-Ar. Conditions: initial concentration of arsenic ions, 10.0 mg dm^{-3}; pH, 6; contact time, 15 h; stirring speed, 200 rpm.

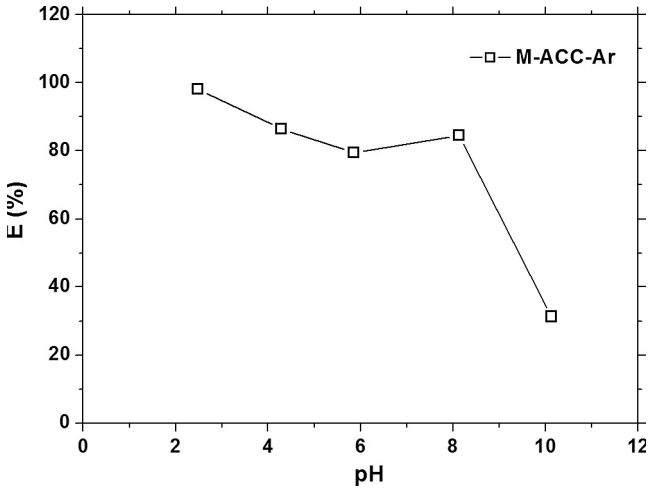

Figure 8 Effect of pH on the adsorption of arsenic ion on the M-ACC-Ar. Conditions: initial concentration of arsenic ions, 10.0 mg dm^{-3}; contact time, 15 h; stirring speed, 200 rpm.

each isotherm models, it is evident that the linear Langmuir plot has the highest correlation coefficient ($R^2 > 0.99$) suggesting that the adsorption occurs through the formation of a monolayer coverage of arsenic ions on the homogenous surface of the M-ACC-Ar. The Langmuir adsorption capacity, q_m, of arsenic ions on the investigated M-ACC-Ar was estimated to be 5.30 mg g^{-1}; this result is in good agreement with the result obtained by nonlinear analysis. Compared to q_m values of carbon-based materials modified by chemical methods of modification (such as impregnation), presented in the literature (Table S1, Supporting information), the importance of such a high removal capacity achieved only by mechanochemical activation of ACC has to be emphasized.

3.2.6. Mechanism of arsenic sorption onto M-ACC-Ar

The mechanism of adsorption of arsenic ions onto M-ACC-Ar was investigated by the (linear and nonlinear) pseudo first- and the second-order kinetic models as well as intraparticle diffusion model. The results of kinetic models are shown in Figs. S3–S5 (Supporting information) and the values of kinetic parameters for adsorption of arsenic ions onto M-ACC-Ar at various initial metal ions concentrations are presented in Table 5. The highest values of calculated correlation coefficients ($R^2 > 0.99$) and good agreement of $q_{e,cal}$ with $q_{e,exp}$, showed that the linear pseudo-second-order model fits better with the experimental data than the pseudo-first order and intraparticle diffusion models which suggest that the chemisorption might be the rate-controlling step of adsorption process.

Carbon-based materials have amphoteric character; thus, their behavior depends on the pH of the solution. Further, it is well known that pH_{PZC} of carbon surfaces depends on the chemical and electronic properties of the surface functional groups and is a good indicator of these properties. The measured pH_{PZC} values of ACC, M-ACC-Air and M-ACC-Ar are 4.46, 5.04 and 5.77, respectively (Fig. S6, Supporting information). The carbons surface is positively charged at $pH < pH_{PZC}$ favoring the adsorption of anionic species and negatively charged at $pH > pH_{PZC}$, which favors the adsorption of cationic species. The different pH_{PZC} values of the three samples indicate that over a particular pH range, different ionic species are formed on the surface of the material, generating different charges on the carbon surface: positive surface charge is produced by dissociation of surface groups of basic character induced mostly in the ACC upon milling in inert atmosphere leading to the increase of pH_{PZC} values. Arsenic can exist in different species H_3AsO_4 (pH 0–4), $H_2AsO_4^-$ (pH 2–8), $HAsO_4^{2-}$ (pH 6–12) and AsO_4^{3-} (10–14). From Fig. 8,

Table 4 Langmuir and Freundlich isotherm parameters obtained by linear and nonlinear fitting for the M-ACC-Ar.

Model	Parameters	Linear	Nonlinear
Langmuir fitting	q_m	5.30	5.16
	K_L	21.61	37.63
	R^2	0.99	0.98
Freundlich fitting	n	4.60	4.60
	K_F	6.25	7.05
	R^2	0.92	0.89

[a] Conditions: pH, 6; adsorbent concentration, 1 g dm^{-3}; and contact time, 15 h.

Table 5 Kinetic parameters for the adsorption of arsenic ions onto M-ACC-Ar at various initial concentrations.[a]

Kinetic model parameters	Initial concentration, C_0 (mg dm^{-3})			
	2.5	5.0	7.5	10.0
Pseudo first-order model				
Linear form				
$q_{e,exp}$ (mg g^{-1})	2.40	4.67	5.50	5.23
$q_{e,cal}$ (mg g^{-1})	0.21	1.30	2.70	1.54
K_{pf} (1 min^{-1})	0.01	0.02	0.01	0.01
R^2	0.64	0.83	0.87	0.92
Nonlinear form				
$q_{e,cal}$ (mg g^{-1})	2.36	3.71	4.72	4.55
K_{pf} (1 min^{-1})	0.07	0.08	0.99	0.56
R^2	0.97	0.58	0.99	0.56
Pseudo second-order model				
Linear form				
$q_{e,exp}$ (mg g^{-1})	2.40	4.67	5.50	5.23
$q_{e,cal}$ (mg g^{-1})	2.41	3.94	5.42	4.97
K_{ps} (1 min^{-1})	0.12	0.03	0.01	0.02
R^2	0.99	0.99	0.99	0.99
Nonlinear form				
$q_{e,cal}$ (mg g^{-1})	2.44	3.83	5.54	4.86
K_{ps} (1 min^{-1})	0.08	0.06	0.01	0.02
R^2	0.95	0.76	0.97	0.88
Intraparticle diffusion model				
K_{id} (mg g^{-1} $min^{-1/2}$)	0.02	0.04	0.20	0.09
a (mg g^{-1})	2.05	3.19	1.64	3.30
R^2	0.54	0.82	0.77	0.91

[a] Conditions: pH, 6; adsorbent concentration, 1 g dm^{-3}; and contact time, 15 h.

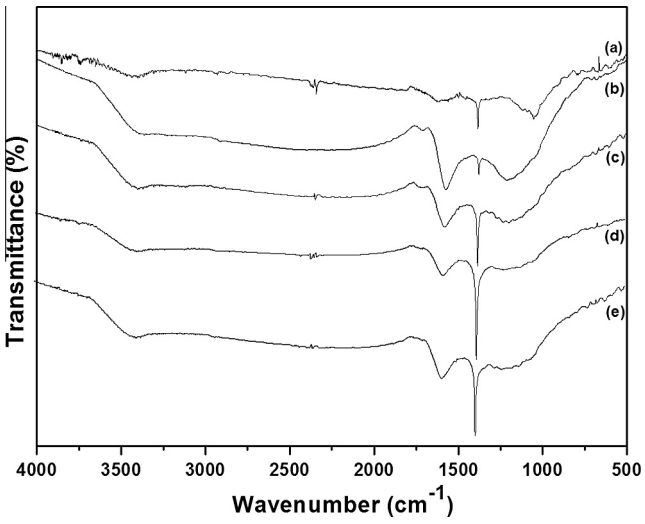

Figure 9 FT-IR spectra of the (a) ACC and (b) M-ACC-Ar before the sorption and M-ACC-Ar after the sorption at pH equal to (c) 2, (d) 6 and (e) 10.

the highest removal efficiencies were obtained in highly acidic conditions.

In order to more deeply understand mechanism of adsorption of arsenic species onto M-ACC-Ar, FTIR spectra of ACC and M-ACC-Ar before and after the sorption at pH equal to 2, 6 and 10 were recorded and studied, Fig. 9. The band assignments are shown in Table 6.

The main difference between the FTIR spectra of ACC and M-ACC-Ar samples (before and after the sorption) lies in the high signal to noise ratio of ACC spectra because the absorption of the fibers is very intense while the concentration of the different functional groups on its surface is relatively low (Saha et al., 2009). Upon milling, more pronounced peaks appear as a consequence of increase in number of acidic and basic groups (which is in accordance with the results of Boehm titration, Table 1). The samples show absorption at approximately 3435 cm^{-1} that corresponds to O—H stretching mode of carboxylic and phenolic groups. Bands that appear at 1585 cm^{-1} and 1383 cm^{-1}, assigned to C—O and C═O, are characteristic for carbon materials and indicate presence of ethers and lactones. Positions of all peaks in spectra remain unchanged upon modification in inert atmosphere except a shift of a broad peak centered at 1045 cm^{-1}, assigned to C—O stretching in phenolic groups (Guedidi et al., 2014) toward higher wave numbers (1220 cm^{-1}). Further, positions of all peaks in the FTIR spectra after the sorption of arsenic ions remain unchanged, indicating that mechanism of sorption cannot be assigned to the ion exchange mechanism. Further, the reduction of the intensity of peaks at 1220 cm^{-1} with increase of pH, and its complete disappearance on pH = 10 (see Fig. 9), indicates that phenolic groups dissociate in highly basic conditions after the sorption of arsenic spices.

Changes in the relative intensities of FTIR peaks at 1215, 1384, 1580 and 1720 cm^{-1}, that are the consequence of (a)symmetric vibrations of COO^- as well as C═C stretching vibrations, indicate changes in electronic densities formed during the adsorption of different arsenic species in the pH range 2–10. Ionic species formed on the M-ACC-Ar upon milling, which have basic character, enable high electron density on the surface. Interactions between the delocalized π electrons of the Lewis basic sites in the basal planes of activated carbon and the free electrons of the arsenic ions indicate dispersive forces to be responsible for adsorption mechanism on pH values higher than pH_{PZC}, where repulsive electrostatic interactions between the anion and negatively charged surface of sample occur. In pH region above pH_{PZC} is the dominant presence of uni-negative H_2AsO^{4-} which has an amphoteric character and can act as an acid:

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$$

The shift of the final pH (pH_f) of the solution toward the acidic region was observed (Fig. 10). The shift of the final pH (pH_f) of the solution toward the acidic region can be also attributed to the amphoteric character of the carbon surface that approximates the pH of a solution to their PZC value. The effect of amphoteric character of the surface can be observed in slight increase in the pH_f at $pH_i \sim 4$.

$HAsO_4^{2-}$ present in the solution between 6 and 12 has lower tendency for interacting with the delocalized π electrons of the Lewis basic sites in the basal planes:

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+$$

leading to the drastic drop in the removal efficiency of arsenic at pH = 10 (Fig. 8).

By decreasing pH of the solution below pH_{PZC} the electrostatic attractions between the positively charged surface and the oxyanions increase the adsorption performance. The reaction pathway can be described as

$$Carbon - OH_2^+ + H_2AsO_4^- \rightarrow carbon - OH_2^+ - H_2AsO_4^-$$
(surface complexation)

Table 6 Band assignments for FTIR spectra of ACC and M-ACC-Ar before the sorption and M-ACC-Ar after the sorption at pH equal to 2, 6 and 10.

Wave number (cm^{-1})	Band assignment	References
3435	—O—H stretching vibration of carboxylic groups and phenolic groups	Saha et al. (2009)
1725–1700	—COOH saturated Carboxylic acids	Saha et al. (2009)
1720	C═O stretching vibration of ketone, and/or aromatic carboxylic groups	Guedidi et al. (2014)
1580–1600	C═C stretching modes of aromatic rings or C═O stretching vibration conjugated with aromatic carboxylic groups	Guedidi et al. (2014)
1384	$—COO^-$ symmetric	Saha et al. (2009)
1000–1250	C—O stretching in phenolic groups	Guedidi et al. (2014)

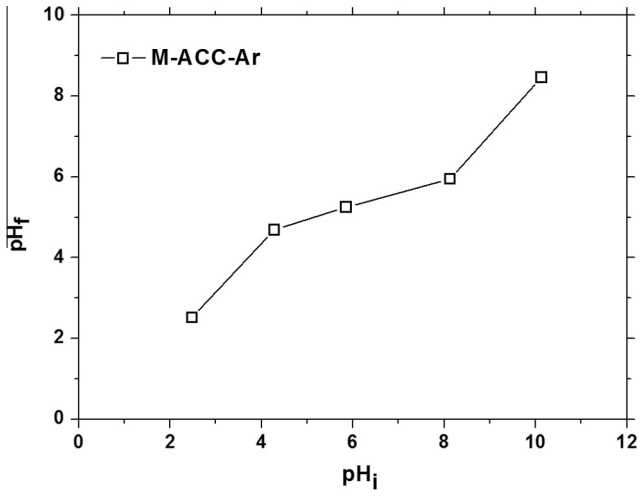

Figure 10 pH change of the solution at the adsorption equilibrium of arsenic ion on the M-ACC-Ar.

As a consequence of this type of interaction no change in pH_f should occurs (Fig. 10). So, slight increase of $pH_f \sim 4$ can be only attributed to the amphoteric character of the carbon surface.

In highly acidic solution (pH = 2), increase in the removal efficiency is a consequence of the highest number of positive charges on the surface of the material that attracts negative arsenic anions.

The results demonstrate the operation of two types of mechanisms: one associated with electrostatic forces and the other with dispersive forces. These types of interactions predominate in basic carbons, since the electron density on the carbon surface is high compared to acid activated carbons (Belhachemi and Addoun, 2012).

4. Conclusions

Mechanochemical modification of the ACC yields in obtaining new carbon materials and consequent significant change in surface properties. Increase in acidic and basic groups occured upon milling in inert and air atmospheres. Approximately 5 times higher number of basic groups is obtained by milling in inert conditions. Morphological and microstructural changes induced upon milling of the M-ACC-Ar were comprehensive and an adsorption occurs through the formation of monolayer coverage of arsenic ions on the homogenous surface of the M-ACC-Ar with maximum adsorption capacity of 5.3 mg g^{-1}. Pseudo second order kinetics and chemisorption is the rate-controlling step of adsorption process. Electrostatic and dispersive interactions between arsenic species and carbon particles are responsible for the mechanism of arsenic removal in pH range from 2 to 10.

By mechanochemical modification of ACC it is possible to prepare new carbons possessing 'tailor-made' properties by simple, environmentally friendly and low cost method that can be widely and easily applied. However, this method of modification changes the cloth structure into the powder form and it represents its big disadvantage. But, mechanochemical modification induced specific changes in the material that were not obtained by any other method used in the literature. This gives the clear guidepost for direction of changes that has to be induced on the surface of the carbon cloth to achieve good arsenic removal ability.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2016.07.004.

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